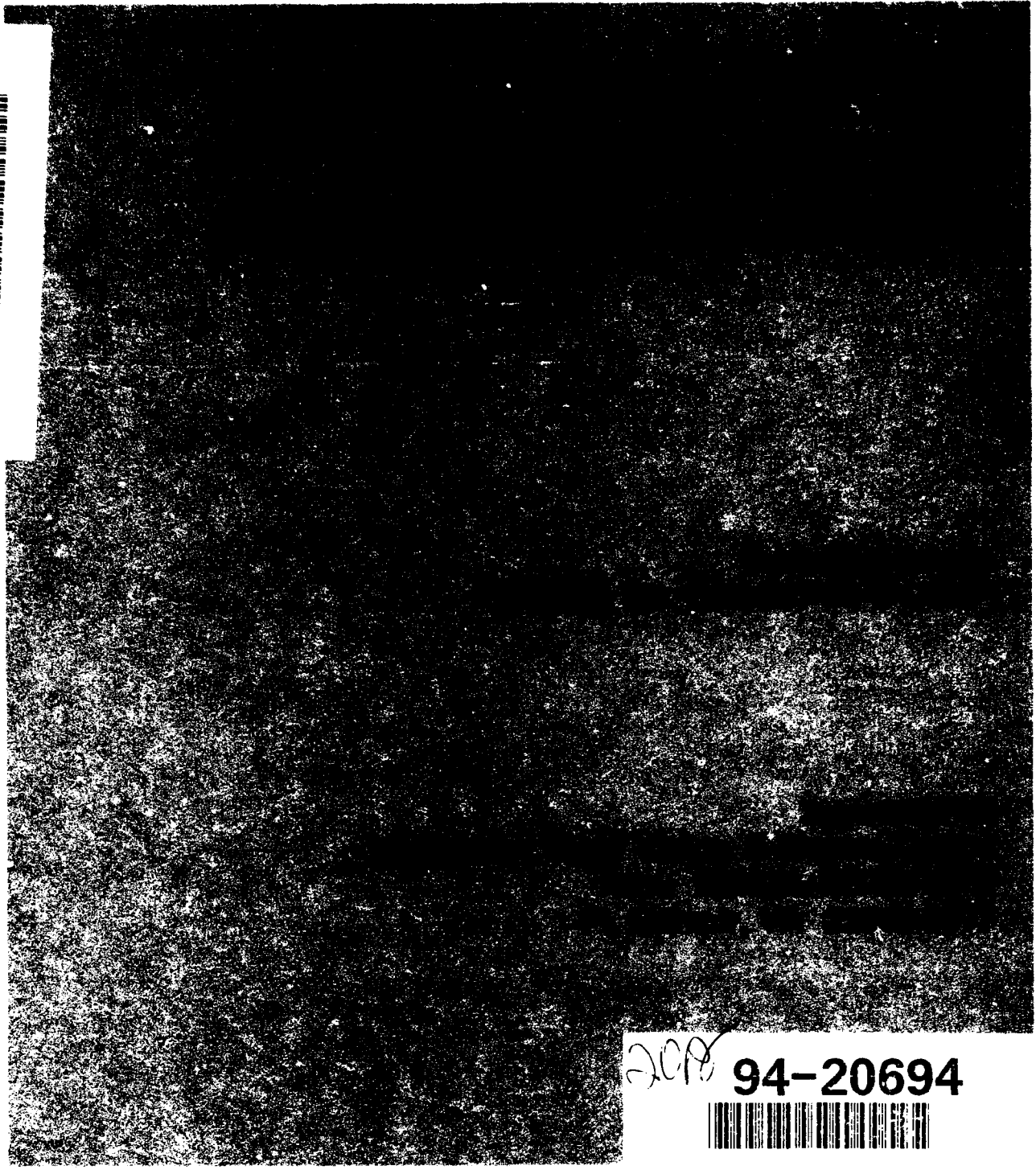


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Final Report for:
EPITAXIAL MOCVD OF THIN FILM CERAMICS
FOR PYROELECTRIC DETECTORS

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TABLE OF CONTENTS

	<u>Page</u>
1 INTRODUCTION	1
2 SUBSTRATE PREPARATION	3
2.1 CoSi ₂	3
2.2 Platinum and Palladium on Si	3
2.3 YBCO on CoSi ₂	3
3 PbTiO ₃ FILM GROWTH	4
4 FILM CHARACTERIZATION	8
4.1 X-ray diffraction	8
4.2 Rutherford Backscattering Spectroscopy	9
4.3 Electrical Measurements	12
5 CONCLUSION	14
6 REFERENCES	14

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LIST OF ILLUSTRATIONS

		<u>Page</u>
1	Pyroelectric detector element	2
2	Surface of CoSi_2 (1000X)	4
3	Surface of YBCO/ CoSi_2 (1000X)	5
4	Schematic diagram of ceramic MOCVD facility at Spire	6
5	Surface of PTO/YBCO/ CoSi_2 under optical microscope (50X and 1000X)	7
6	X-ray diffraction θ -2 θ scan for PTO/YBCO/ CoSi_2 and YBCO/ CoSi_2 structures ...	8
7	Rutherford backscattering spectroscopy data from PTO/ CoSi_2	9
8	RBS data for the PTO/YBCO/ CoSi_2 multilayer	10
9	RBS data for PTO/Pd/Si	11
10	Depth distribution for Pb, Ti, O, Pd, and Si calculated from RBS data of Figure 9	12
11	Temperature dependence of capacitance of PTO/YBCO/ CoSi_2 capacitor	13

LIST OF TABLES

		<u>Page</u>
I	Estimated room temperature dielectric constants of PTO on various bottom electrodes	13

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ABSTRACT

The objective of this research was to deposit epitaxial thin films of PbTiO_3 (PTO) on CoSi_2 films on Si wafers, using metalorganic chemical vapor deposition (MOCVD). This is a first step towards integration of PbTiO_3 -based pyroelectric detectors with semiconducting electronics. It is expected that epitaxial or strongly aligned films of the active pyroelectric material will yield larger polarization, and thus larger detector response, than polycrystalline material. In addition, thin films have a lower thermal mass than bulk crystals used in current technology, resulting in a faster response to radiation. The sensitivity will be enhanced by separating the detector from the underlying silicon wafer. Spire demonstrated MOCVD of PbTiO_3 on CoSi_2 by using a diffusion barrier between the two films.

Spire prepared heteroepitaxial CoSi_2 films on Si wafers, and deposited thin films of PTO on these substrates by MOCVD. In the absence of a diffusion barrier, Pb from PTO diffuses into the CoSi_2 layer and even into the underlying Si substrate. The resulting Pb-Ti-O films did not show any trace of the expected crystal structure and were electrically conducting, making it impossible to measure the dielectric constant and polarization. A diffusion barrier had to be found, with the additional requirement that it should allow highly oriented growth of the entire layer sequence. Spire selected the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO), which can be grown in a highly oriented fashion on CoSi_2 and is a good electrode for PbTiO_3 -based compounds. Researchers at the MIT Magnet Laboratory grew a film of YBCO by laser ablation on epitaxial CoSi_2 . Spire then deposited a thin film of PTO on this structure by MOCVD. X-ray diffraction analysis of the resulting stack of films revealed peaks associated with the crystal structures of CoSi_2 , YBCO and PTO. Small capacitors were made and the dielectric constant K of the PTO film was measured as a function of temperature up to 400°C . The temperature dependence of K is as expected.

Despite initial difficulties, we have shown that crystalline PbTiO_3 can be grown on CoSi_2 using a suitable diffusion barrier.

1 INTRODUCTION

Pyroelectric infrared detectors are in widespread use by DoD because of simplicity of construction and room temperature operation. The ultimate goal of this research is to develop a thin film technology for pyroelectric detectors with potential of integration with standard semiconductor technology. Currently, pyroelectric detectors are made with a hybrid technology, in which crystals of the pyroelectric material are cut, polished and bonded to an integrated circuit die containing the readout electronics.¹ The technology is relatively expensive and unsuited for large scale integration, because detector elements are larger than typical integrated circuit devices. In addition, this method imposes limits on the response time of the detector because of the relatively high thermal mass of the crystals. An integrated thin film technology is expected to improve response time and integration, while simplifying the manufacturing process.

To increase the response speed and sensitivity, the thermal mass and thermal losses of the detector must be as small as possible. This implies the use of thin films (a few 1000Å to a few μm) for the active part of the detector and thermal isolation from the underlying substrate. The approach proposed by Spire is to use a SIMOX (separation by implantation of oxygen) wafer, where the surface silicon layer is a single crystal epitaxially oriented with respect to the substrate, but electrically isolated from it by an oxide layer. This single crystal silicon layer is then converted to single crystal cobalt-silicide by ion implantation and annealing.² As cobalt-silicide is a good conductor and is chemically stable in the presence of oxygen, it serves as a substrate and back-contact for heteroepitaxial growth of the pyroelectric film.

A second important feature allowed by the choice of SIMOX is the possibility to thermally isolate the sensor element as shown in Figure 1, using selective etching methods similar to those used in silicon micromachining. After deposition, the pyroelectric film and the top contact layer are patterned and openings down to the SiO_2 are made next to the detector element. The exposed oxide layer is then isotropically etched in a solution which is slow to attack CoSi_2 or pure Si. The material underneath the sensing element can be completely removed, leaving a thin membrane of top contact/pyroelectric/cobalt-silicide supported on two edges. The sensing element is thus very well isolated thermally and becomes more sensitive.

For demonstration of feasibility in Phase I, Spire proposed to use the pyroelectric and ferroelectric material PbTiO_3 (lead-titanate, or PTO), to be grown by metalorganic chemical vapor deposition (MOCVD). The choice of material was based on available know-how rather than optimum performance in the final device. MOCVD is a versatile deposition method that can be directly integrated with semiconductor manufacturing. The objective of Phase I was to address the following questions:

- Can MOCVD yield epitaxial PTO films on polycrystalline CoSi_2 ?
- Can PTO be deposited epitaxially on CoSi_2 -on-Si?
- Is the pyroelectric coefficient of epitaxial PTO greater than that of polycrystalline PTO?

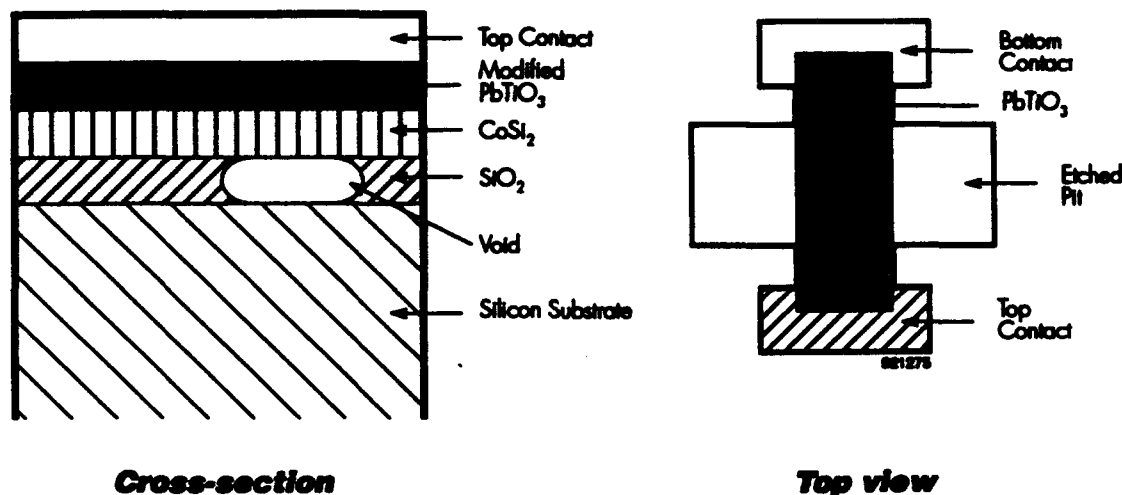


Figure 1 *Pyroelectric detector element.*

Spire Corporation successfully answered these questions. PTO cannot be grown epitaxially directly on CoSi_2 due to chemical interactions and interdiffusion of metallic species. PTO can, however, be grown on CoSi_2 -on-Si with the help of a suitable conductive diffusion barrier. Spire showed that the high temperature superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) in its non-superconducting, metallic state constitutes such a barrier, with potential for highly oriented growth. The change of the dielectric constant of MOCVD-grown PTO on YBCO/ CoSi_2 as a function of temperature showed the expected variation.

The experimental results of this program are described in detail below. Presentation is organized according to the tasks in the statement of work:

Task 1 - polycrystalline and heteroepitaxial CoSi_2 films were to be prepared on silicon wafers.

Task 2 - PTO was to be deposited epitaxially by MOCVD on the substrates prepared in Task 1.

Task 3 - the films grown in Task 2 were to be characterized in terms of structure, composition, and pyroelectric/ferroelectric properties.

2 SUBSTRATE PREPARATION

2.1 CoSi₂

The first task was to prepare heteroepitaxial CoSi₂ on silicon wafers by high dose ion implantation and annealing. A 100 mm <111> silicon wafer, nominally 0.004Ω-cm, was introduced into an ion implanter and mounted on carbon supports for thermal insulation. This technique allows the wafer to be heated directly by the intense ion beam current. The wafer was implanted with Co⁺ at 90 keV to a total dose of 2×10^{17} ions/cm² at a beam current of 500 μA. The ion beam was rastered over the wafer for uniformity. After implantation, the wafer was annealed in a furnace in N₂ for two hours at 900°C.

The surface of the wafer after processing was smooth and visibly very uniform in color and appearance. The silicide made ohmic contact to the substrate. RBS analysis showed that the cobalt-silicide layer had the right stoichiometry (CoSi₂) and that the top surface was the silicide and not residual silicon. X-ray diffraction confirmed that the silicide was epitaxial to the underlying Si. The wafer was cut into rectangular pieces (1 x 2 cm²) for further depositions.

One piece of the wafer was introduced into the MOCVD reactor and heated to 730°C in 12 torr of an O₂/Ar mixture identical to that used for PTO deposition (O₂ flow of 200 sccm; Ar flow of 4500 sccm). Microscopic examination of the CoSi₂ showed no change, as expected.

2.2 Platinum and Palladium on Si

For quality control purposes, we decided to grow PTO films on more familiar substrates. A conducting layer is needed under the PTO to allow measurement of the polarization, both for characterization purposes and for the final pyroelectric device. Because of the high temperatures and oxidizing environment needed for PTO growth, platinum and palladium had been chosen for the electrodes in earlier programs. One batch of silicon wafers was oxidized and coated with a thin (about 200Å) layer of Ti, followed by 1500Å of Pt. The Ti is to provide a sticking layer for Pt; in its absence, the Pt layer tends to peel away after PTO deposition. Another batch of silicon wafers was coated directly with 3000Å of Pd.

2.3 YBCO on CoSi₂

We quickly realized (see Section 4) that significant interaction was taking place between the PTO and CoSi₂, and the need for a further diffusion barrier became apparent. In addition to being a conductor, the ideal barrier should allow epitaxial growth of PTO. The high temperature superconducting oxide YBa₂Cu₃O_{7.8} (YBCO), a metallic conductor with a resistivity of a few hundred μΩ-cm above its superconducting transition, fulfills these requirements. It has been successfully grown in a highly oriented manner on CoSi₂,^{3,4} and has been used as an electrode for PTO.⁵

YBCO films were deposited by laser ablation by Dr. J. S. Moodera, researcher at the MIT Magnet Laboratory. A target of sintered, stoichiometric YBa₂Cu₃O_{7.8} was ablated by the focussed beam of a frequency-tripled Nd-YAG laser operated in a pulsed mode (10 Hz). The ablation was carried out in a vacuum chamber in an ambient of 200 mtorr of O₂. The CoSi₂/Si substrates were

attached to a heater block with silver paste. In a first run, the heater was at 720°C, the optimum temperature for YBCO deposition on SrTiO₃ substrates. However, the resulting films were extremely rough and insulating, suggestive of a chemical reaction between YBCO and CoSi₂. A second deposition at the lower temperature of 650°C was successful, resulting in specular, conducting YBCO films. Examination of the surface under an optical microscope showed a distribution of micron-sized particles on a smooth background (Figure 2). X-ray diffraction revealed only peaks associated with CoSi₂ and YBCO. However, no preferential orientation was found for the YBCO. Films from the second run, about 2500Å thick, were used for subsequent PTO deposition.

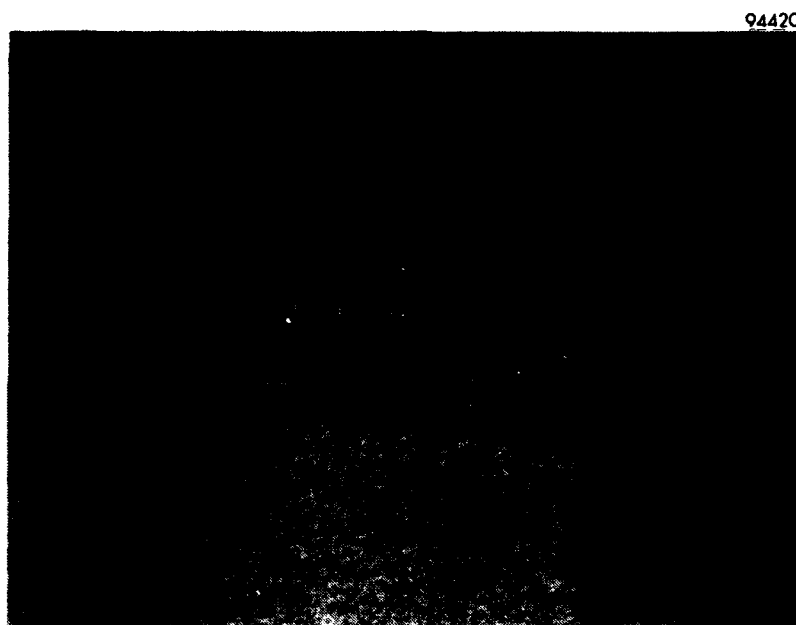


Figure 2 *Surface of CoSi₂ (1000X).*

3 PbTiO₃ FILM GROWTH

The objective of Task 2 was to grow PbTiO₃ epitaxially on CoSi₂ by MOCVD. The lattice constant of CoSi₂ is 5.36Å, a near match to Si (5.43Å), but about 20% mismatched to PTO (tetragonal at room temperature, with $c = 4.15\text{\AA}$ and $a = 3.91\text{\AA}$). The difference in lattice constants is expected to be compensated by strain in very thin films and by defects in thicker films.

The MOCVD apparatus used for the growth of PTO is shown in Figure 3. This facility controls precisely the temperature and ratio of reactants in the deposition zone to fabricate a film of the desired stoichiometry and structure.



Figure 3 *Surface of YBCO/CoSi₂ (1000X).*

Precise flows of a carrier gas such as argon, F_c , are fed into a liquid bubbler. The bubbler is maintained at a constant pressure, P_b . If the flow rate is not too high, the carrier gas becomes saturated with the vapor of the source in thermal equilibrium. The vapor pressure of the source material in the bubbler, P_m , is sensitive to temperature. To maintain accurate and reproducible mass flow of material, the source bubblers are kept at a fixed temperature, T_m , within $\pm 0.01^\circ\text{C}$, by water or oil baths. The mass flow of metal vapor now delivered to the reactor is given by:

$$F_m = F_c P_m / (P_b - P_m)$$

The source gases, diluted with the carrier gas, flow into the reactor, which is maintained at a different fixed pressure by sensors and feedback-controlled throttling valves. Oxidant, such as oxygen but possibly nitrous oxide or water vapor, is pushed into the reactor through a separate inlet to prevent interactions in the manifold. High temperature source materials, such as zirconium trifluoro-acetylacetonate, can be introduced through another port to prevent premature decomposition at the temperature required for transport of some materials.

The reactor can be heated to a high temperature by rf induction when the pressure is over 0.1 atmosphere (76 torr). At lower pressure, as was the case for this research, the susceptor is changed and heated electrically (resistive wiring) because the gas would form a plasma in the induction field. Temperature is accurately controlled by immersed thermocouples, calibrated with optical pyrometers.

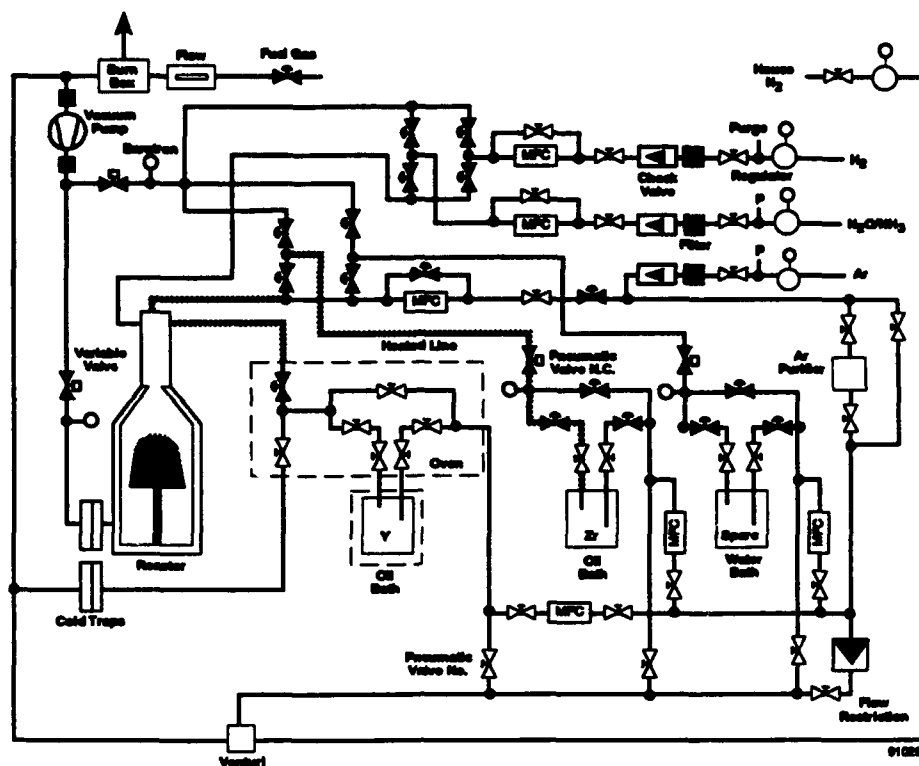


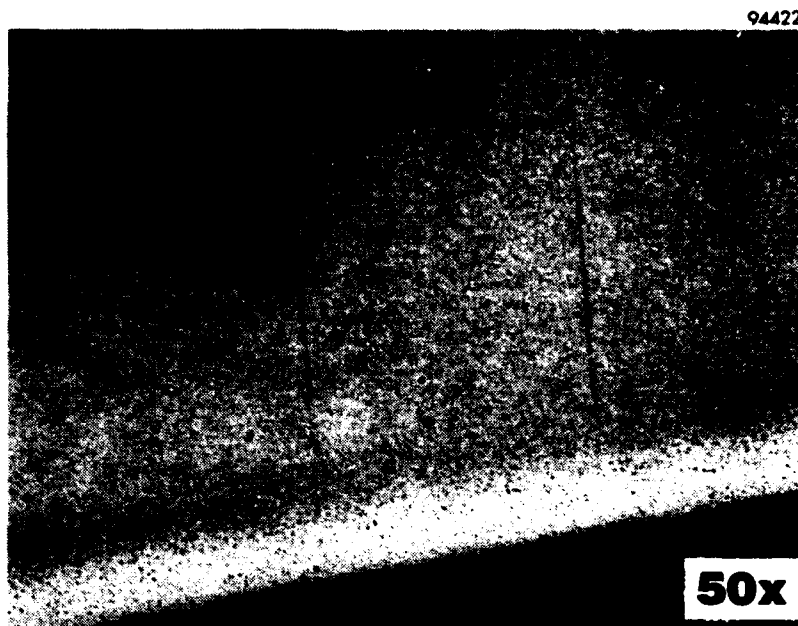
Figure 4 Schematic diagram of ceramic MOCVD facility at Spire.

For this task, the original choice of deposition parameters was that found to be optimum in an earlier DoD program to deposit $\text{Pb}(\text{Zr,Ti})\text{O}_3$ on Si.⁶ While this choice is not necessarily optimum for the new substrate materials, nor for the requirements of epitaxial growth, it served as a starting point. The chemicals were tetraethyl-lead for the lead source chemical, titanium-isopropoxide for the titanium source, oxygen as the oxidant, and argon as the carrier. The reactor chamber pressure was set at 12 torr, with a total flow rate of 5000 sccm. Bubbler temperatures and flows were set respectively at 90°C and 590 sccm for Ti and 38°C and 140 sccm for Pb.

Thin films of PbTiO_3 were grown on CoSi_2 at 550°C and 730°C. Rutherford backscattering (RBS) analysis showed interdiffusion of the PTO and CoSi_2 . X-ray diffraction did not show any signs of crystalline PbTiO_3 , while showing weak CoSi_2 peaks. A further indication of chemical interaction between PTO and CoSi_2 was the fact that the PTO top layer was slightly conducting, and not insulating as required.

The same bubbler temperatures and flow rates were used for PTO growth on YBCO/ CoSi_2 . Because depositions of YBCO on CoSi_2 above 700°C were found to cause reaction and interdiffusion, a lower temperature of 600°C was chosen for the subsequent PbTiO_3 deposition as well. The resulting film was grey, optically smooth and mirror-like. Figure 5 shows the film surface as seen through an optical microscope under (a) 50x and b) 1000x magnification. Part of the YBCO/ CoSi_2 was masked during the deposition to allow subsequent electrical measurements (lower right corner of Figure 5a). A distribution of particulates (typically a few microns in size) is visible on both the YBCO and PTO. Comparison to Figure 3, YBCO alone, suggests that most particulates were present before PTO deposition, most likely the result of the laser ablation process. The underlying film appears smooth.

a.)



b.)

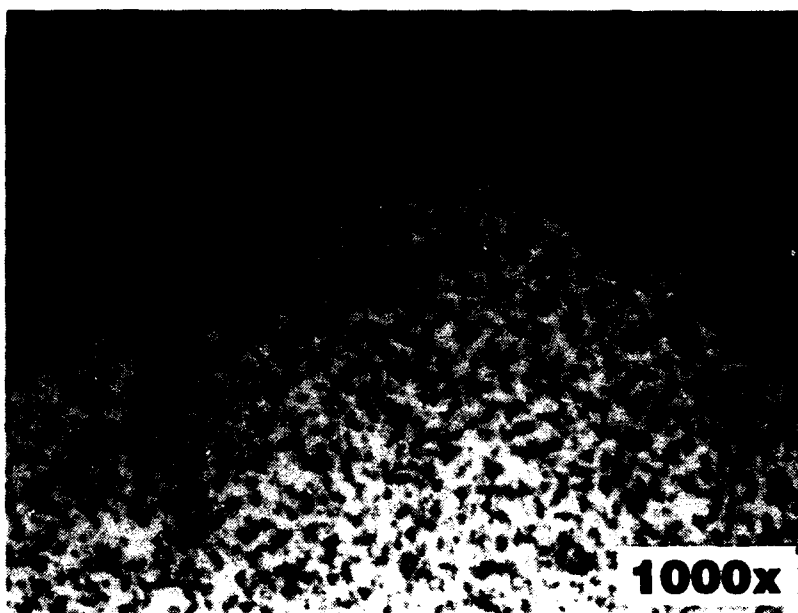


Figure 5 *Surface of PTO/YBCO/CoSi₂ under optical microscope (50X and 1000X).*

PTO films were also grown on Pt and Pd films on silicon wafers described in the previous section. Insulating, optically smooth, grey-green films were obtained.

4 FILM CHARACTERIZATION

4.1 X-ray Diffraction

X-ray diffraction of PTO films deposited directly on CoSi_2 failed to reveal any structure associated with PTO, although peaks corresponding to CoSi_2 were seen.

X-ray diffraction of the PTO/YBCO/ CoSi_2 structure revealed peaks associated with CoSi_2 , YBCO, and PTO, without foreign phases (Figure 6, where the scan of YBCO/ CoSi_2 is shown for comparison). Peaks associated with PTO in the (101), (110), (200) and (111) orientation are seen, as are (002) and (110) YBCO peaks. Neither YBCO nor PTO showed strong preferential orientation. The PTO lattice constants calculated from the positions of the diffraction peaks are close to $a = 3.95\text{\AA}$ and $c = 4.05 - 4.1\text{\AA}$, suggesting a reduced tetragonality compared to single crystals. This may be due to strain resulting from lattice mismatch with YBCO/ CoSi_2 . It is not unusual for thin films to show different crystal structure than corresponding single crystals; for instance, BaTiO_3 films have been reported to grow in a cubic rather than a tetragonal phase under certain conditions.⁷

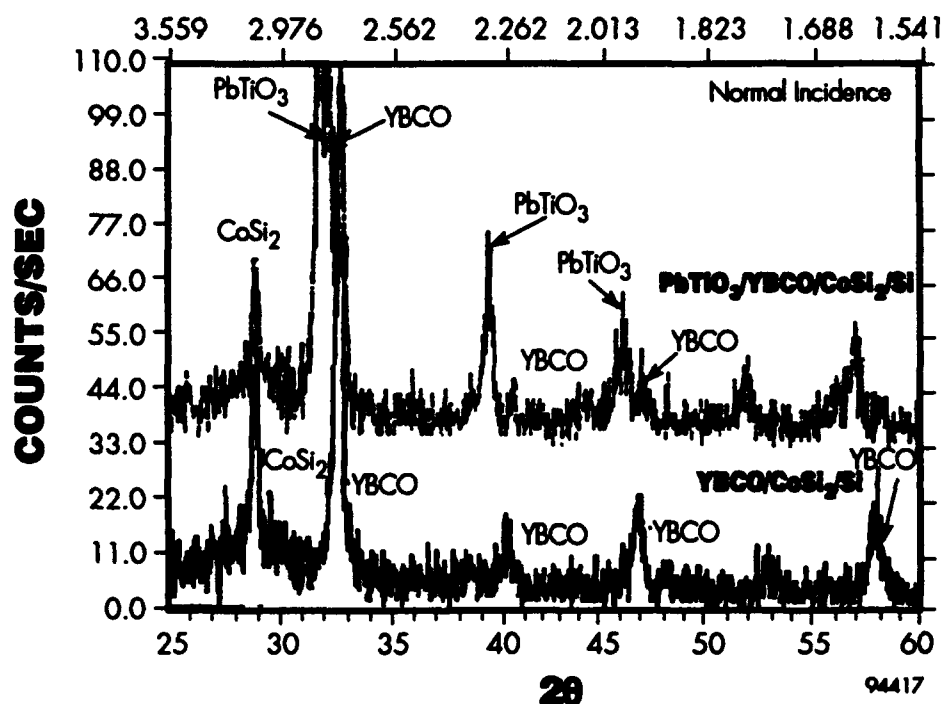


Figure 6 X-ray diffraction θ - 2θ scan for PTO/YBCO/ CoSi_2 and YBCO/ CoSi_2 structures.

The fact that the PTO shows no preferential orientation is certainly due to the fact that the underlying YBCO is not preferentially oriented. It should be possible to remedy this problem. Indeed, highly c-axis oriented growth of YBCO on CoSi_2 , both by laser ablation and by MBE, has been reported. However, the time constraints of the Phase I program limited our effort to only two depositions at different substrate temperatures. Further optimization of YBCO deposition parameters should allow us to obtain improved orientation, which would be revealed by the absence of peaks other than (00n) in an X-ray diffraction scan similar to Figure 6. A higher degree of orientation of the YBCO film is expected to translate into a more strongly oriented PTO film; epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ has been grown on epitaxial YBCO/ SrTiO_3 , while YBCO/MgO resulted in polycrystalline $\text{Pb}(\text{Zr,Ti})\text{O}_3$.⁵

4.2 Rutherford Backscattering Spectroscopy

For PTO films directly deposited on CoSi_2 at low deposition temperatures (450 to 550°C), the Pb:Ti ratio was close to 1:1, as it should be. However, the lead was found to diffuse into the underlying silicide and even into the substrate. At higher temperatures (750°C), the lead content at the surface falls off, presumably due to the high volatility of lead oxide at this temperature. Channeling measurements showed that the initial epitaxial relation between the silicide and the underlying silicon was lost after the PbTiO_3 deposition. Figure 7 shows RBS data for PTO/ CoSi_2 .

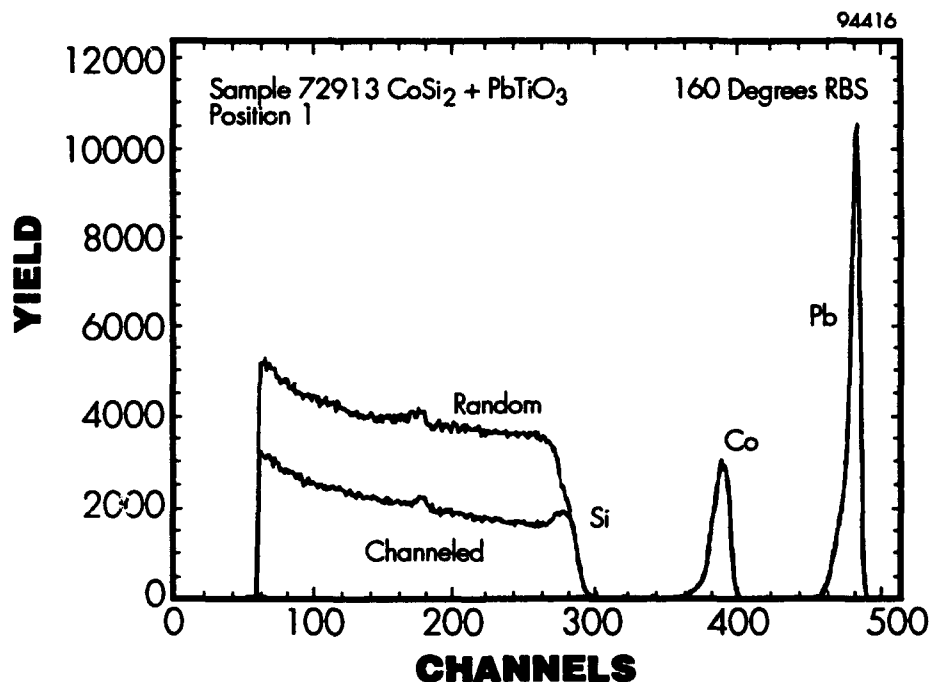


Figure 7 *Rutherford backscattering spectroscopy data from PTO/ CoSi_2 .*

RBS measurements were performed on the PTO/YBCO/CoSi₂ structure (Figure 8). Because of overlapping peaks, the interpretation is not straightforward, and exact stoichiometries are difficult to extract. Satisfactory fits were obtained with the following parameters:

PTO - 3900Å, Pb:Ti:O = 1:0.9:4.2 (ideally 1:1:3; large uncertainty on O)

YBCO - 2400Å, Y:Ba:Cu:O = 0.9:2:3.5:9 (ideally 1:2:3:7)

CoSi₂ - 780Å, Co:Si = 1:2 (ideal ratio)

Comparison of the fit with the data suggests some (limited) interdiffusion between Pb (from PTO) and Ba (from YBCO), but very little between CoSi₂ and YBCO.

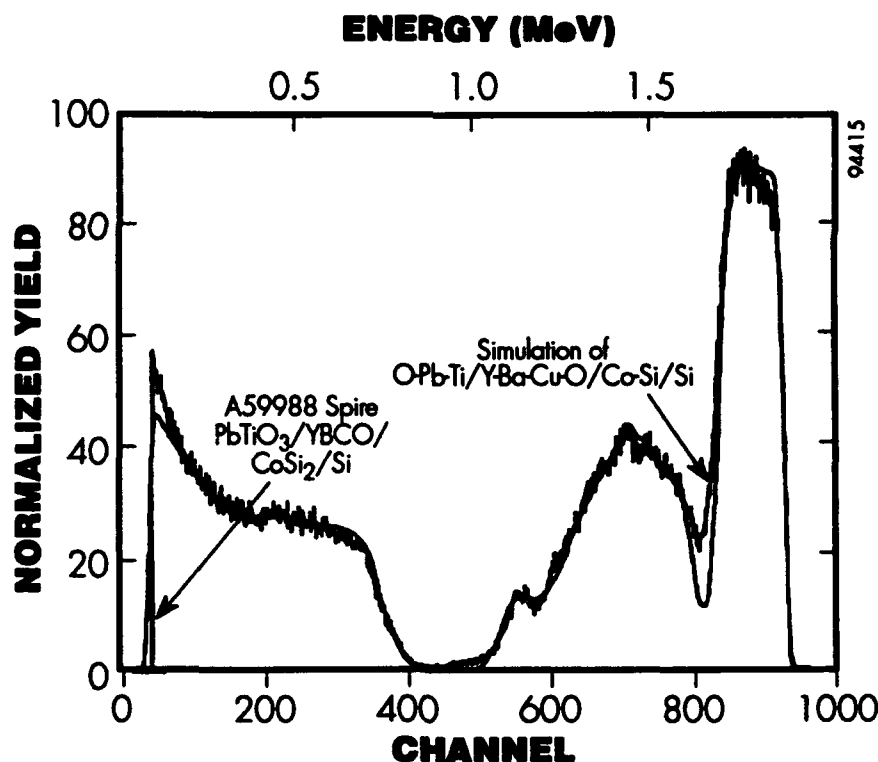


Figure 8 RBS data for the PTO/YBCO/CoSi₂ multilayer.

Figure 9 shows the RBS spectrum of PTO on Pd/Si, and Figure 10 shows the calculated depth profile. This film was deposited at 550°C. While there is a region of stoichiometric composition about 600Å thick, the film is lead-poor at the surface, while showing at the same time lead diffusion into the palladium electrode. This is very similar to what was observed at slightly higher deposition temperature on CoSi₂. The data also show intermixing between Pd and Si.

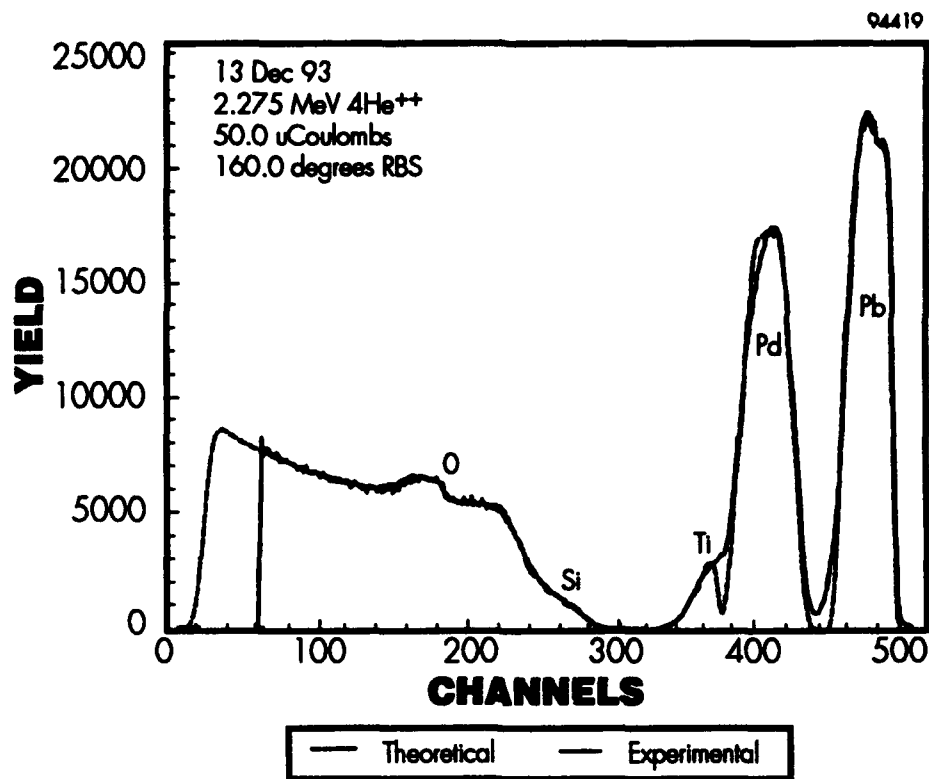


Figure 9 RBS data for PTO/Pd/Si.

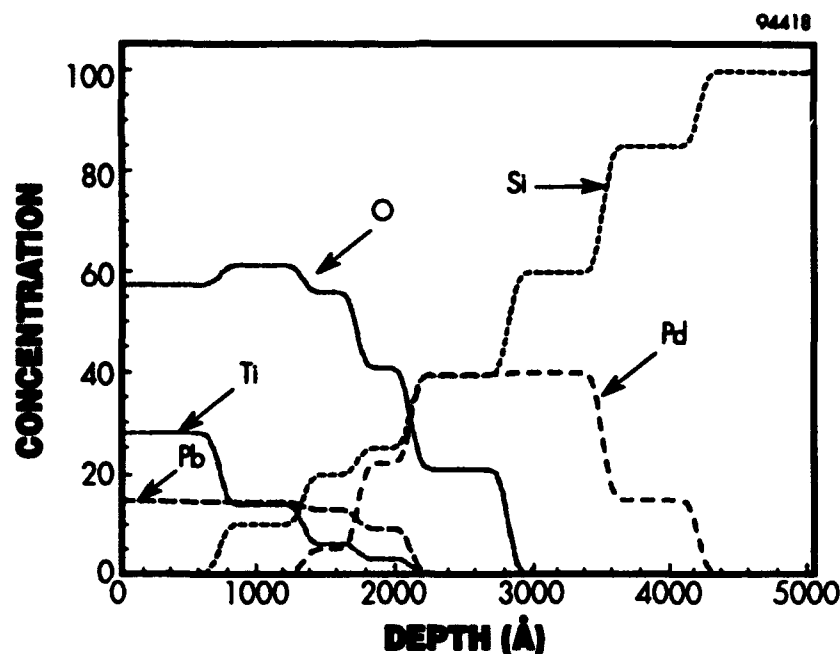


Figure 10 Depth distribution for Pb, Ti, O, Pd, and Si calculated from RBS data of Figure 9.

4.3 Electrical Measurements

The YBCO/CoSi₂ under the PTO was conducting, while the top PTO layer was insulating when measured with a multimeter on a 20 MΩ scale, which translates to a resistivity at least in the 10⁸ Ω cm range. A few small dots (diameter 500 μm) of metallic AuGe alloy were sputtered onto the PTO layer through a shadow mask to allow measurement of the dielectric properties. Capacitance of these dots was measured at room temperature and up to 400°C on a hot plate. The capacitance was about 70 to 80 pF, and increased with increasing temperature to about 160 pF (see Figure 11). The increase was significant between 350°C and 40°C, as is expected from a ferroelectric with a Curie temperature of 490°C. However, the hot plate was not powerful enough to reach the Curie point. The dielectric constant computed from the capacitance and the thickness determined by RBS (4000 Å) is only about 20 at room temperature, and no remanent polarization was observed when the capacitor was measured in a Sawyer-Tower circuit. The reason for the low effective dielectric constant in the structure is not clear. Attempts to hot-pole the film did not improve the electrical properties. The reason for this behavior may have to do with strain due to mismatch with YBCO, or insufficient crystallinity, or an insulating layer between the conducting YBCO and PTO which has a low dielectric constant. In the last case, most of the electric field is across the low permittivity layer, decreasing the effective capacitance. Optimized growth conditions are expected to improve ferroelectric properties of PbTiO₃/YBCO/CoSi₂.

Small capacitors were fabricated with the films grown on Pt and Pd electrodes as for the film grown on YBCO/CoSi₂. The dot sizes were, however, smaller (200 μm diameter). On Pt, the capacitance was typically close to 500 pF for a 8000Å thick film, while films deposited on Pd yielded smaller capacitance (60 pF for 2000Å). Figure 11 shows the temperature variation of the capacitance of PTO on platinum. As for the PTO/YBCO/CoSi₂, the capacitance increases with temperature, as expected. The polarization loops were open, indicative of hysteresis, but could not be saturated. The value of the remanent polarization inferred from the loops was an order of magnitude lower than the value reported for single crystals. This is not unexpected for unpoled PTO.

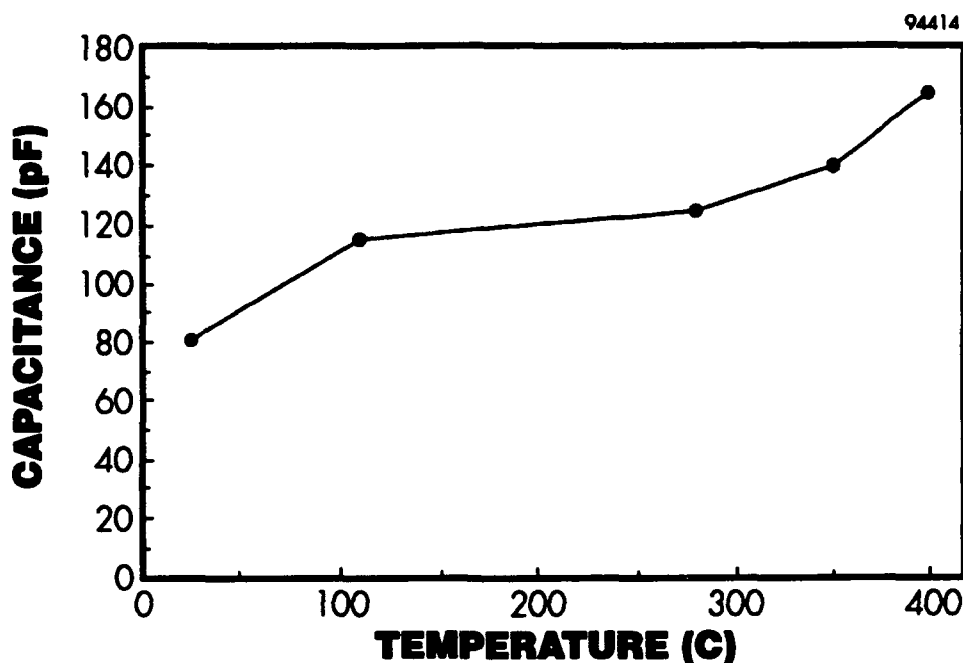


Figure 11 *Temperature dependence of capacitance of PTO/YBCO/CoSi₂ capacitor.*

Table I summarizes the estimated room temperature dielectric constants based on the capacitance measurements.

Table I *Estimated room temperature dielectric constants of PTO on various bottom electrodes.*

Electrode	Estimated Dielectric Constant
Pt	>100
YBCO	20
Pd	60

5 CONCLUSION

The need for a diffusion barrier between CoSi_2 and PTO has become clear in the course of this research. The requirement of maintaining conducting properties during the PTO deposition at 550 to 700°C in a few torr of oxygen poses stringent constraints on the barrier material. The barrier should also allow conservation of the epitaxy of CoSi_2 up to the PTO layer, or at least allow the growth of strongly oriented material.

We have demonstrated that a thin film of YBCO on top of CoSi_2 allows subsequent growth of polycrystalline PTO. The improvement over direct deposition is dramatic even with a non-optimized process. Ferroelectric and pyroelectric properties of these films, though inferred by the temperature variation of the permittivity, could not be measured directly, suggesting either strain, incomplete crystallization or presence of a low-permittivity second phase at the YBCO-PTO interface. Optimization of deposition conditions in Phase II is expected to yield epitaxial or highly c-axis oriented YBCO films on CoSi_2 , followed by epitaxial or highly c-axis oriented PbTiO_3 films with superior pyroelectric properties.

The demonstration that highly quality thin films of PbTiO_3 can be grown on CoSi_2 -on-silicon brings us one step closer to achieving the enhanced sensitivity predicted for thermally isolated, thin film pyroelectric detectors.⁸ The technology has the potential to yield a new generation of highly sensitive, dense, room-temperature-operated detector arrays with both civilian and military applications, such as mobile weapon sights and driver's aids.

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